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Composition comprising a monomer compound exhibiting an optical property, method making use of said composition, a monomer compound, a polymer containing  
5 said monomer compound and the use thereof

The present invention relates to novel cosmetic or pharmaceutical compositions, especially for topical application, and especially to novel makeup  
10 compositions, comprising organic polymers with particular optical properties and especially fluorescence properties.

The present invention also relates to novel monomeric  
15 compounds with optical properties, especially fluorescence properties, and also to polymers that may be prepared from these compounds.

Cosmetic compositions, and especially makeup  
20 compositions such as loose or compact powders, foundations, makeup rouges, eyeshadows, lipsticks or nail varnishes, generally consist of a suitable vehicle and one or more coloring agents intended to give said compositions a certain color before and/or after  
25 applying them to the skin, mucous membranes, semimucous membranes and/or the integuments such as the nails, the eyelashes or the hair.

To create colors, a fairly limited range of coloring  
30 agents is used at the present time, especially comprising lakes, mineral pigments, organic pigments and nacreous pigments. The pigments and lakes used in the makeup field are of very diverse origin and chemical nature. Their physicochemical properties,  
35 especially their granulometry, specific surface area, density, etc., are thus very different. These differences are reflected by variations in behavior: their ease of use or of dispersion in the medium; their light and heat stability; their mechanical properties.

Mineral pigments, in particular mineral oxides, are, on the other hand, very stable to light and to pH, but give rather dull, pale colors. It is thus necessary to introduce a large amount of them into cosmetic formulations in order to obtain a sufficiently saturated mark. This high percentage of mineral particles can, however, affect the gloss of the composition. As regards nacreous pigments, they can produce varied colors, but of relatively weak intensity, which lead to iridescent effects that are usually quite weak. In the field of temporary or short-term hair dyeing, which gives rise to a slight change in the natural color of the hair that holds from one shampoo wash to the next and that serves to enhance or correct an already-established shade, coloration with common pigments to give the hair a temporary tint has already been proposed, but the shades obtained by this coloration remain quite dull, too uniform and rather boring.

20 In the field of makeup, only organic lakes have made it possible until now to obtain bright, vivid colors. However, most organic lakes have very poor lightfastness, which is reflected by pronounced  
25 attenuation of their color over time. They may also be heat- and/or pH-unstable. Furthermore, certain lakes produce excessive bleeding, i.e. they have the drawback of staining the support onto which they are applied. Thus, this may have the consequence of staining ocular  
30 lenses in the case of eyeliners or mascaras, or of leaving a coloration on the skin or the nails after makeup removal in the case of lipsticks or nail varnishes. Finally, the instability of lakes is also worsened when they are combined with photoreactive  
35 pigments, for instance titanium dioxide. Now, as it happens, these pigments are very widely used in makeup, especially for protecting against UV radiation. Consequently, the use of organic lakes in cosmetics is quite limited, which has the consequence of limiting

the shades that may be produced.

Thus, there is still a need for organic polymers with optical properties, which can be used in cosmetics, to  
5 give compositions comprising them and/or makeup obtained using these compositions adequate optical effects, said polymers moreover having good heat and photochemical stability, while at the same time producing little bleeding.

10

After considerable research, the Applicant has demonstrated that the use of a specific family of polymers, in fact comprising at least one specific monomer, unexpectedly allows such a result to be  
15 obtained.

Thus, one subject of the invention is a cosmetic or pharmaceutical composition comprising, in a physiologically acceptable medium, at least one polymer  
20 comprising at least one monomeric compound as defined below.

Another subject of the invention is a cosmetic process for making up or caring for keratin materials,  
25 especially bodily or facial skin, the lips, the nails, the eyelashes, the eyebrows and/or the hair, comprising the application of such a cosmetic composition to said materials.

30 The polymers according to the invention may be in solid or liquid form and give noteworthy optical effects to the compositions comprising them and also to the applied makeup; in particular, they can give lightening or color effects.

35

These optical effects may be advantageously modified as a function of the chemical nature and/or the position of the various substituents present on the monomer with an optical effect used to form the polymer. In general,

when the group X is an oxygen, the resulting monomer will rather be of yellow/orange color; when the group X comprises a nitrogen atom, the resulting monomer will rather be in the red range.

5

Among the other advantages that the polymers according to the invention can afford, mention may be made of their good heat, pH and light stability.

10 It has also been found that the polymers according to the invention show good solubility in fatty substances, which can vary and be adjusted according to the nature of the monomers. This good liposolubility can also facilitate their subsequent use, especially in cosmetic  
15 compositions generally comprising a fatty phase.

Furthermore, the good cosmetic properties of the compositions according to the invention are maintained when they comprise the polymers according to the  
20 invention.

Furthermore, although being of similar chemical structure, the polymers according to the invention may show, depending on the nature of the substituents, a  
25 wide variety of optical effects, which may range from yellow to red/violet. This gives access to a range of compounds, belonging to the same chemical family, and thus being formulated in a similar manner, which offer noteworthy diversities of colors or of optical  
30 properties; this especially facilitates the task of formulators by allowing them to keep a common architecture for all of their compositions, irrespective of the polymers with optical properties used.

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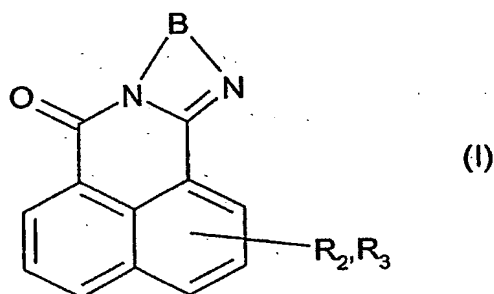
Moreover, it has been found that the monomers according to the invention, and the polymers comprising them, have good fluorescence properties. It is recalled that fluorescent compounds absorb in the ultraviolet and

visible range, and re-emit energy by fluorescence at a wavelength of between 380 nm and 830 nm.

In addition, the polymers according to the invention  
5 have the advantage of easily undergoing makeup removal.

The composition according to the invention thus comprises, in a physiologically acceptable medium and especially a cosmetically or pharmaceutically  
10 acceptable medium, at least one polymer that can be obtained by polymerization, especially free-radical polymerization, of at least one monomer of formula (I).

Said monomer of formula (I) thus corresponds to the  
15 following formula:



in which:

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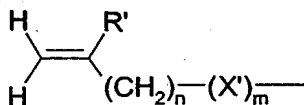
-  $R_2$  and  $R_3$ , which are present on the same ring or each on a different ring, represent, independently of each other, a hydrogen, a halogen or a group of formula -X-G-P (II), with the proviso that at least one of the  
25 radicals  $R_2$  and/or  $R_3$  represents a group of formula (II), in which:

- X is chosen from the groups -O-, -S-, -SO-, -SO<sub>2</sub>-, -NH- and -NR- with R representing a linear, branched  
30 and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 30 carbon atoms, optionally substituted with one or more groups chosen

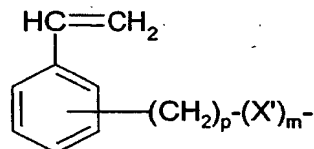
5 - G is a linear, branched and/or cyclic, saturated and/or unsaturated divalent carbon-based radical containing 1 to 32 carbon atoms, optionally substituted with one or more groups chosen from =O; OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one  
10 or more heteroatoms chosen from O, N, P, Si and S;

$$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} = \text{C} - \text{R}' \\ \diagup \\ \text{H} \end{array} \quad \begin{array}{c} \text{O} \\ \parallel \\ \text{C} - (\text{X}')_m \end{array}$$

(IIa)



(111b)



(IIIc)

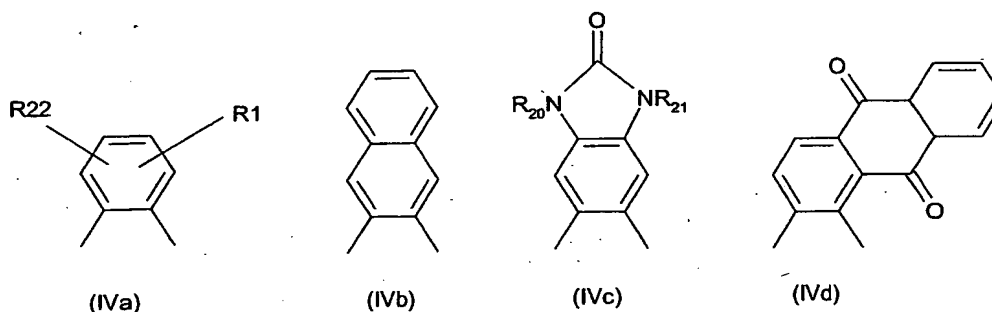
in which:

- R' represents H or a linear or branched, saturated C<sub>1-6</sub> hydrocarbon-based radical,

- X' represents O, NH or NR" with R" representing a radical chosen from C<sub>1-6</sub> alkyl, C<sub>6-10</sub> aryl, (C<sub>6-10</sub>)-aryl(C<sub>1-6</sub>)alkyl and (C<sub>1-6</sub>)alkyl(C<sub>6-10</sub>)aryl radicals, the alkyl and/or aryl groups also possibly being substituted with one or more groups chosen from OH, halogen, C<sub>1-6</sub> alkoxy and C<sub>6-10</sub> aryloxy; preferably, X' represents O;

- m is equal to 0 or 1; n is equal to 0 or 1; p is  
30 equal to 0, 1 or 2; and

- B represents one of following divalent aromatic groups (IVa) to (IVd):



in which:

- R1 is a linear, branched and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 32 carbon atoms, optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S;
- R22 is a hydrogen atom or a linear, branched and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 32 carbon atoms, optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S;
- R20 and R21 are, independently of each other, a hydrogen atom, a linear or branched C1-8 alkyl radical or a cyclopentyl, cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, benzyl, naphthyl or phenyl radical.

It will be noted that some of the compounds for which, simultaneously, P is of formula (IIIa), X' is O, m = 1, X is NH and B is of formula (IVc) may be known.

In the present invention, the term "cyclic radical" means a monocyclic or polycyclic radical, which is thus itself in the form of one or more saturated and/or unsaturated, optionally substituted rings (for example cyclohexyl, cyclodecyl, benzyl or fluorenyl), but also a radical that comprises one or more of said rings (for example p-tert-butylcyclohexyl or 4-hydroxybenzyl).

In the present invention, the term "saturated and/or unsaturated radical" means totally saturated radicals, totally unsaturated radicals, including aromatic radicals, and also radicals comprising one or more double and/or triple bonds, the rest of the bonds being single bonds.

$R_2$  is preferably a hydrogen atom, and  $R_3$  is thus a group of formula (II).

In said group of formula (II), X is preferably chosen from -O-, -NH- and -NR- with R preferentially representing a linear, branched and/or cyclic, saturated or unsaturated hydrocarbon-based radical optionally comprising a hydrocarbon-based ring that is itself saturated or unsaturated, containing 2 to 18 and especially 3 to 12 carbon atoms, optionally substituted with one or more groups chosen from =O, OH,  $NH_2$  and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S.

R may especially be an ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, hexyl, cyclohexyl, octyl, cyclooctyl, decyl, cyclodecyl, dodecyl, cyclododecyl, phenyl or benzyl radical.

Preferentially, X is chosen from -NH- and -NR- with R representing a cyclohexyl.

However, when X is equal to NR, then B is preferably different than formula (IVa).

The divalent radical G is preferably a linear, branched and/or cyclic, saturated or unsaturated divalent hydrocarbon-based radical optionally comprising a hydrocarbon-based ring that is itself saturated or unsaturated, containing in total 2 to 18 and especially 3 to 10 carbon atoms, optionally substituted with one



or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P and Si.

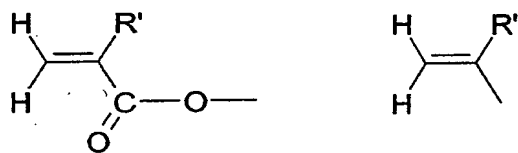
5 Preferentially, G is chosen from linear or branched, saturated divalent hydrocarbon-based radicals optionally comprising a saturated hydrocarbon-based ring, containing in total 2 to 18 and especially 3 to 10 carbon atoms.

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Thus, G may be chosen from ethylene, n-propylene, isopropylene (or 1-methylethylene and 2-methylethylene), n-butylene, isobutylene, pentylene, especially n-pentylene, hexylene, especially  
15 n-hexylene, cyclohexylene, heptylene, octylene, cyclooctylene, decylene, cyclodecylene, cyclohexyldimethylene especially of formula -CH<sub>2</sub>-C<sub>6</sub>H<sub>10</sub>-CH<sub>2</sub>-, dodecylene and cyclododecylene radicals.

20 In formula (IIIb), if n = 0, then, preferably, m = 0.

The polymerizable group P is preferably chosen from one of the following formulae:



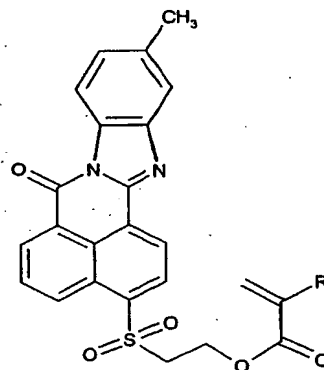
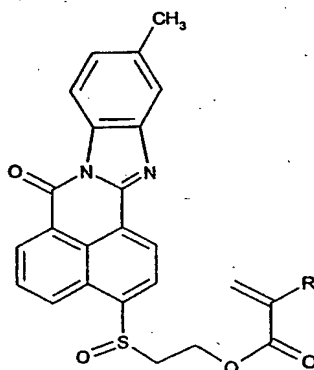
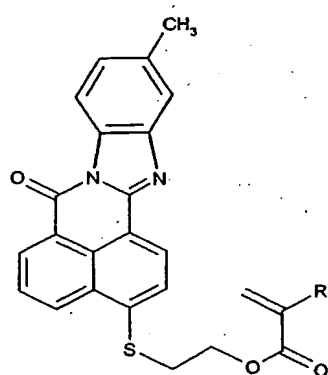
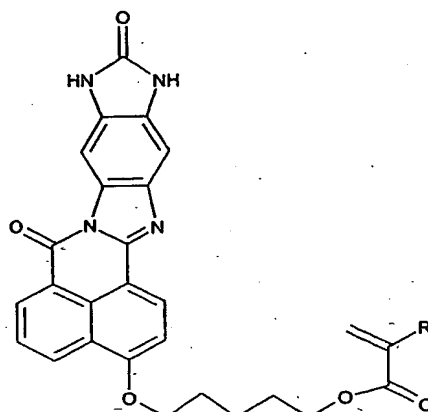
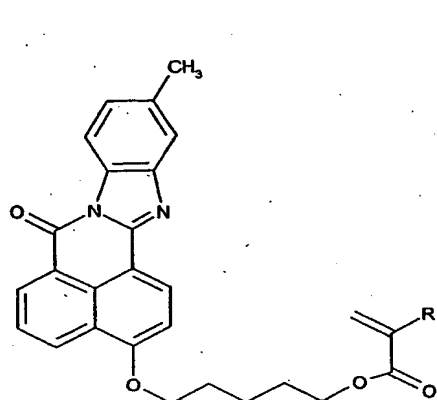
in which R' represents H or methyl.

The group B is preferably chosen from those of formula  
30 (IVa) in which R<sub>1</sub> is preferentially a linear, branched and/or cyclic, saturated carbon-based radical containing 1 to 32 carbon atoms, especially 2 to 12 or even 3 to 6 carbon atoms; in particular, R<sub>1</sub> may be a methyl, ethyl or propyl radical.

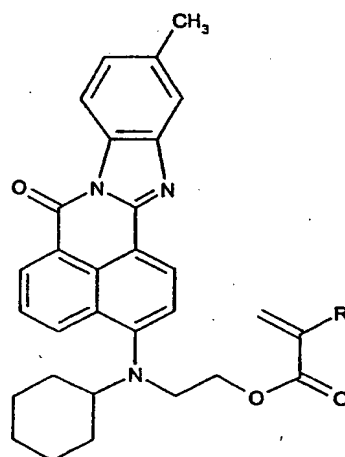
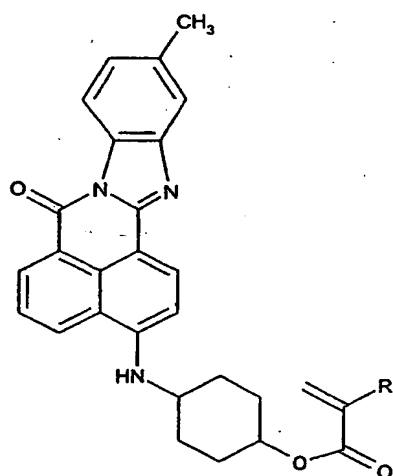
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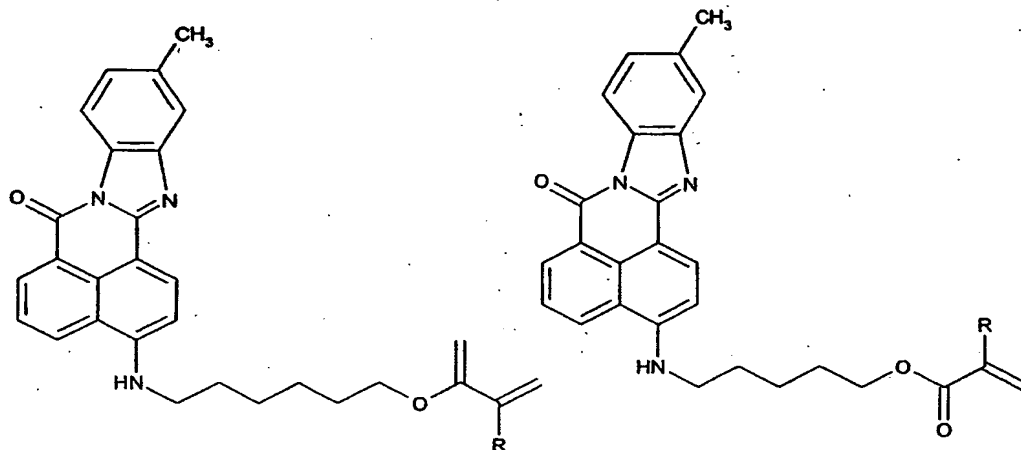
Among the monomeric compounds that are particularly

preferred according to the invention, mention may be made of the compounds corresponding to one of the following formulae, in which R is hydrogen or methyl:

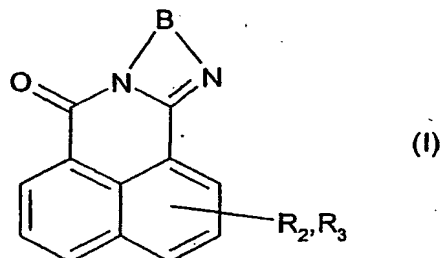


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Another subject of the present invention is a monomeric compound of formula (I), as defined below:



5

in which:

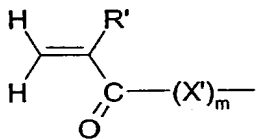
-  $R_2$  and  $R_3$ , present on the same ring or each on a  
 10 different ring, represent, independently of each other,  
 a hydrogen, a halogen or a group of formula  $-X-G-P$   
 (II), with the proviso that at least one of the  
 radicals  $R_2$  and/or  $R_3$  represents a group of formula  
 (II), in which:

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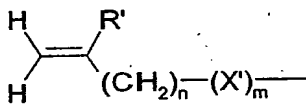
-  $X$  is chosen from  $-O-$ ,  $-S-$ ,  $-SO-$ ,  $-SO_2-$ ,  $-NH-$  and  $-NR-$   
 groups with  $R$  representing a linear, branched and/or  
 cyclic, saturated and/or unsaturated carbon-based  
 radical containing 1 to 30 carbon atoms, optionally  
 20 substituted with one or more groups chosen from  $=O$ ,  $OH$ ,  
 $NH_2$  and halogen atoms; and/or optionally interrupted  
 with one or more heteroatoms chosen from  $O$ ,  $N$ ,  $P$ ,  $Si$   
 and  $S$ ;

- G is a linear, branched and/or cyclic, saturated and/or unsaturated divalent carbon-based radical, containing 1 to 32 carbon atoms, optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S;

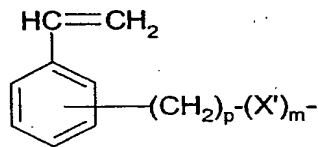
- P is a polymerizable group chosen from one of the following formulae:



(IIIa)



(IIIb)



(iii c)

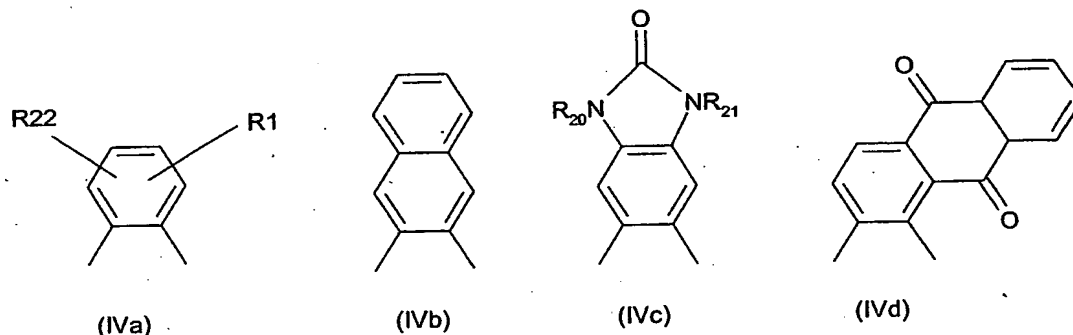
in which:

15 - R' represents H or a linear or branched, saturated  
C<sub>1-6</sub> hydrocarbon-based radical,

- X' represents O, NH or NR" with R" representing a radical chosen from C<sub>1-6</sub> alkyl, C<sub>6-10</sub> aryl, (C<sub>6-10</sub>)-aryl(C<sub>1-6</sub>)alkyl and (C<sub>1-6</sub>)alkyl(C<sub>6-10</sub>)aryl radicals, the alkyl and/or aryl groups also possibly being substituted with one or more groups chosen from OH, halogen, C<sub>1-6</sub> alkoxy and C<sub>6-10</sub> aryloxy; preferably, X' represents O;

25 - m is equal to 0 or 1; n is equal to 0 or 1; p is  
equal to 0, 1 or 2; and

- B represents one of the following divalent aromatic groups (IVa) to (IVd):



in which:

- R1 is a linear, branched and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 32 carbon atoms, optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms;
  - R22 is a hydrogen atom or a linear, branched and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 32 carbon atoms, optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S;
  - R20 and R21 are, independently of each other, a hydrogen atom, a linear or branched C1-8 alkyl radical or a cyclopentyl, cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, benzyl, naphthyl or phenyl radical;
- with the exclusion of the compounds for which, simultaneously, P is of formula (IIIa), X' is O, m = 1, X is NH and B is of formula (IVc).

Another subject of the invention is a polymer comprising at least one such monomeric compound.

Another subject of the invention is the use of such a monomeric compound or of such a polymer comprising it, in a composition, for giving said composition optical effects, especially fluorescence effects.

The novel monomers, and the polymers comprising them, have good optical properties and can be prepared more

easily than those of the prior art..

For the purpose especially of industrial exploitation,  
monomeric and polymeric compounds of high reactivity  
5 are sought, which allows a short reaction  
(polymerization) time.

Monomers and polymers that have good optical  
properties, with a wide color range, and which can be  
10 used in cosmetics are also sought.

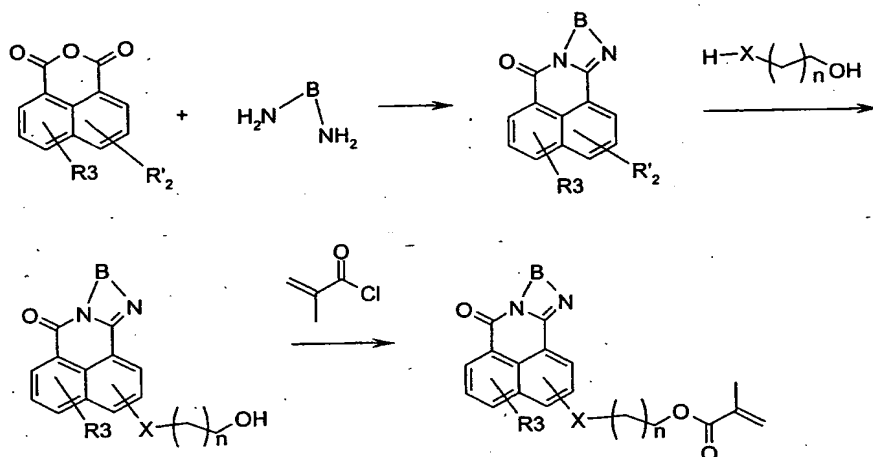
It is found that with the compounds according to the  
present invention, the polymerization is easier,  
especially on account of the presence of a spacer group  
15 (G)..

In addition, the polymers and monomeric compounds  
according to the invention find a most particular use  
for giving a composition optical effects, especially  
20 fluorescence effects.

Some of these compounds may especially be prepared  
according to the prior art, for example according to  
the teaching of document EP 728 745, in particular the  
25 compounds for which X is N.

Schematically, the general synthetic process, for the  
compounds for which X is O or S, may be represented as  
follows:

30



The appropriate naphthalic anhydride may thus be reacted with an appropriate primary diamine.

5

Preferably, the diamine is present in slight excess relative to the naphthalic anhydride, especially in a proportion of from 1 to 1.5 equivalents and preferably 1.1 equivalents per 1 equivalent of anhydride.

10

The reaction may be performed in a solvent chosen from solvents in which the anhydride is soluble, and especially toluene, xylene, acetic acid or NMP; the reaction is preferably performed at the reflux temperature of the solvent, for example at a temperature of 50-250°C and preferably 80-160°C.

15

The isoquinolinone formed can then be reacted with a diol, an amino alcohol or a thio alcohol.

20

For example, when R'<sub>2</sub> is a halogen (preferably chlorine or bromine), it is possible to perform an aromatic nucleophilic substitution, for example using a diol or a thio alcohol, such as 1,3-propanediol, 1,5-propanediol or 2-mercaptoethanol, optionally in alkali metal (for example sodium) alkoxide form.

25

The reaction may be performed in the absence of

solvent, or in the presence of a dipolar aprotic solvent such as dichloromethane or THF (tetrahydrofuran), especially at a temperature of 20-150°C.

5 Sulfur-containing derivatives may then be oxidized under mild conditions so as to give the corresponding sulfoxide. By modifying the oxidation conditions, it is also possible to prepare the corresponding sulfone. These sulfides, sulfoxides and sulfones may then be  
10 converted in order to obtain the desired methacrylates or acrylates.

As regards the alcohol derivatives, they may be reacted with a (meth)acryloyl halide, especially a chloride, so  
15 as to form the corresponding (meth)acrylate.

This reaction may be performed in the presence of a base such as triethanolamine, in a solvent such as tetrahydrofuran or dichloromethane, especially at a temperature of from -30°C to 100°C and preferably 0 to  
20 80°C.

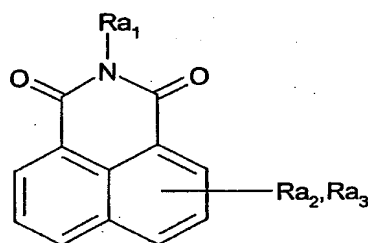
These monomeric compounds may be used as first monomer to prepare copolymers comprising them.

25 In particular, the monomeric compounds with an optical effect according to the invention may be used to prepare homopolymers or copolymers comprising only monomeric compounds with an optical effect of formula (I), alone or as a mixture, or alternatively of formula  
30 (I) as a mixture with others, especially as a mixture with those of formula A and/or B as defined below, these various compounds then each possibly being present, for example, in a proportion of from 0.5% to 99.5% by weight, especially 5% to 95% by weight or even  
35 10% to 90% by weight, and better still each in a proportion of 30% to 70% by weight relative to the total weight of the polymer. This may especially make it possible to prepare polymers with a wide range of optical effects (especially color, optical brightening

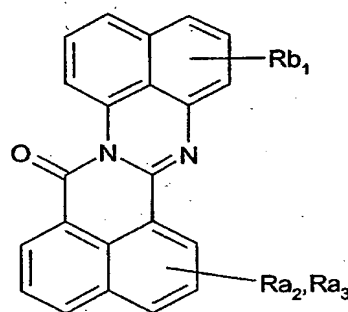


or the like).

Among the monomeric compounds with an optical effect that may be copolymerized with the monomeric compounds of formula (I), and optionally with one or more of the additional comonomers as defined below, mention may be made of the compounds of formula (A) and/or of formula (B) below:



(A)

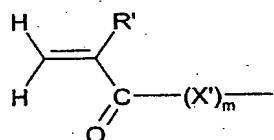


(B)

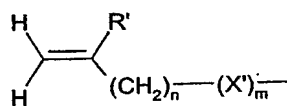
in which:

- Ra1 represents a linear, branched and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 32 carbon atoms; optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S;
- Rb1 is chosen from (i) a hydrogen atom, (ii) a halogen atom, (iii) a linear, branched and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 12 carbon atoms, optionally substituted with one or more groups chosen from =O, OH and NH<sub>2</sub> and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S; (iv) a group NRR' with R and R' being, independently of each other, a hydrogen atom or a linear, cyclic or branched, saturated C1-6 hydrocarbon-based radical, especially methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl or hexyl;

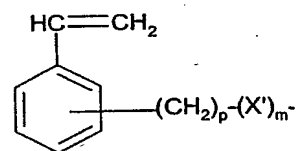
- Ra2 and Ra3, which are present on the same ring or each on a different ring, represent, independently of each other, a hydrogen, a halogen or a group of formula -Xa-Ga-Pa (II), with the proviso that at least one of the radicals Ra2 and/or Ra3 represents a group of formula (II), in which:
- Xa is chosen from the groups -O-, -S-, -SO-, -SO<sub>2</sub>-, -NH- and -NR<sub>4</sub>- with R<sub>4</sub> representing a linear, branched and/or cyclic, saturated and/or unsaturated carbon-based radical containing 1 to 30 carbon atoms, optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S;
  - Ga is a linear, branched and/or cyclic, saturated and/or unsaturated divalent carbon-based radical containing 1 to 32 carbon atoms, optionally substituted with one or more groups chosen from =O, OH, NH<sub>2</sub> and halogen atoms; and/or optionally interrupted with one or more heteroatoms chosen from O, N, P, Si and S;
  - Pa is a polymerizable group chosen from one of the following formulae:



(IIIa)



(IIIb)



(IIIc)

in which:

- R' represents H or a linear or branched, saturated C1-6 hydrocarbon-based radical,
- X' represents O, NH or NR'' with R'' representing a radical chosen from C1-6 alkyl, C6-10 aryl, (C6-10)aryl(C1-6)alkyl and (C1-6)alkyl(C6-10)aryl radicals, the alkyl and/or aryl groups also possibly being substituted with one or more groups chosen from OH, halogen, C1-6 alkoxy and C6-10 aryloxy; and

- m is equal to 0 or 1; n is equal to 0 or 1; p is equal to 0, 1 or 2.

The copolymers according to the invention may be  
5 statistical, alternating or grafted, or block, for  
example diblock or triblock, copolymers, comprising  
said monomeric compounds with an optical effect  
according to the invention and additional comonomers.  
The monomeric compounds according to the invention may  
10 form all or part of a block, or even several blocks.  
Block copolymers of the type A-B, ABA, BAB or ABC in  
which A is a block comprising the monomeric compound(s)  
according to the invention may thus be prepared,  
optionally as a mixture with additional comonomers, B  
15 and C being different blocks, comprising additional  
comonomers, alone or as a mixture, and identical to or  
different than the comonomers present in the block A.

The copolymers comprising the monomeric compounds  
20 according to the invention may also be of the gradient  
type.

In these copolymers, the monomeric compounds with an  
optical effect may be present in an amount of from  
25 0.01% to 70% by weight relative to the weight of the  
final polymer, especially in an amount of from 0.1% to  
50% by weight, in particular from 0.5% to 30% by weight  
or even from 1% to 20% by weight and better still from  
2% to 10% by weight, the additional comonomers, alone  
30 or as a mixture, representing the remainder to 100% by  
weight.

The copolymers according to the invention may comprise,  
in addition to the monomeric compound(s) with an  
35 optical effect, at least one additional comonomer that  
is hydrophilic, or a mixture of such comonomers.

These hydrophilic comonomers may be present in a  
proportion of from 1% to 99.99% by weight, especially

2-70% by weight, better still 5-50% by weight or even 10-30% by weight, relative to the total weight of the copolymer.

5 In the present description, the term "hydrophilic monomer" will denote, without preference, monomers whose homopolymers are soluble or dispersible in water, or of which one ionic form is soluble or dispersible in water.

10

A homopolymer is said to be water-soluble if it forms a clear solution when it is in solution at 5% by weight in water, at 25°C.

15 A homopolymer is said to be water-dispersible if, at 5% by weight in water, at 25°C, it forms a stable suspension of fine, generally spherical particles. The mean size of the particles constituting said dispersion is less than 1  $\mu\text{m}$  and more generally ranges between 5  
20 and 400 nm and preferably from 10 to 250 nm. These particle sizes are measured by light scattering.

A monomer will be said to be "hydrophobic" if it is not hydrophilic.

25

Preferably, the additional hydrophilic comonomer(s) has a  $T_g$  of greater than or equal to 20°C and especially greater than or equal to 50°C, but may optionally have a  $T_g$  of less than or equal to 20°C.

30

The copolymers according to the invention may comprise at least one additional hydrophobic comonomer, or a mixture of such comonomers.

35 These additional hydrophobic comonomers may be present in a proportion of from 1% to 99.99% by weight, especially 30-98% by weight, better still 50-95% by weight or even 70-90% by weight relative to the total weight of the copolymer.

Preferably, the hydrophobic comonomer has a Tg of greater than or equal to 20°C and especially greater than or equal to 30°C, but may optionally have a Tg of less than or equal to 20°C.

In the present invention, the Tg (or glass transition temperature) is measured according to ASTM standard D3418-97, by differential thermal analysis (DSC "Differential Scanning Calorimetry") on a calorimeter, over a temperature range of between -100°C and +150°C at a heating rate of 10°C/minute in 150 µl aluminum crucibles.

In general, as additional comonomer that may be copolymerized with at least one monomeric compound of formula (I), mention may be made, alone or as a mixture, of the following monomers:

- (i) ethylenic hydrocarbons containing from 2 to 10 carbons, such as ethylene, isoprene or butadiene;
- (ii) the (meth)acrylates of formula:

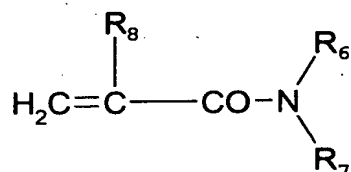


in which R'<sub>3</sub> represents:

- a linear or branched alkyl group of 1 to 18 carbon atoms, in which is (are) optionally intercalated one or more heteroatoms chosen from O, N, S and P; said alkyl group also possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms (Cl, Br, I and F), and groups Si(R<sub>4</sub>R<sub>5</sub>), in which R<sub>4</sub> and R<sub>5</sub>, which may be identical or different, represent a C<sub>1</sub> to C<sub>6</sub> alkyl group or a phenyl group; R'<sub>3</sub> may especially be a methyl, ethyl, propyl, n-butyl, isobutyl, tert-butyl, hexyl, ethylhexyl, octyl, lauryl, isooctyl, isodecyl, dodecyl, cyclohexyl, t-butyl-cyclohexyl or stearyl group; 2-ethylperfluorohexyl; or a C<sub>1-4</sub> hydroxyalkyl group such as 2-hydroxyethyl,

- 2-hydroxybutyl or 2-hydroxypropyl; or a (C<sub>1-4</sub>)alkoxy(C<sub>1-4</sub>)alkyl group such as methoxyethyl, ethoxyethyl or methoxypropyl,
- a C<sub>3</sub> to C<sub>12</sub> cycloalkyl group such as an isobornyl group,
- a C<sub>3</sub> to C<sub>20</sub> aryl group such as a phenyl group,
- a C<sub>4</sub> to C<sub>30</sub> aralkyl group (C<sub>1</sub> to C<sub>8</sub> alkyl group) such as 2-phenylethyl, t-butylbenzyl or benzyl,
- a 4- to 12-membered heterocyclic group containing one or more heteroatoms chosen from O, N and S, the ring being aromatic or non-aromatic,
- a heterocycloalkyl group (1 to 4 C alkyl), such as furfurylmethyl or tetrahydrofurfurylmethyl,
- said cycloalkyl, aryl, aralkyl, heterocyclic or heterocycloalkyl groups possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms and linear or branched C<sub>1-4</sub> alkyl groups in which is (are) optionally intercalated one or more heteroatoms chosen from O, N, S and P, said alkyl groups also possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms (Cl, Br, I and F), and groups Si(R<sub>4</sub>R<sub>5</sub>), in which R<sub>4</sub> and R<sub>5</sub>, which may be identical or different, represent a C<sub>1</sub> to C<sub>6</sub> alkyl group or a phenyl group,
- R'<sub>3</sub> may also be a group -(C<sub>2</sub>H<sub>4</sub>O)<sub>m</sub>-R'', with m = 5 to 150 and R'' = H or C<sub>1</sub> to C<sub>30</sub> alkyl, for example -POE-methyl or -POE-behenyl;

- (iii) the (meth)acrylamides of formula:

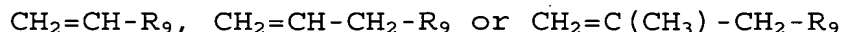


- in which R<sub>8</sub> denotes H or methyl; and R<sub>7</sub> and R<sub>6</sub>, which may be identical or different, represent:
- a hydrogen atom; or

- a linear or branched alkyl group of 1 to 18 carbon atoms, in which is (are) optionally intercalated one or more heteroatoms chosen from O, N, S and P; said alkyl group also possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms (Cl, Br, I and F), and groups  $\text{Si}(\text{R}_4\text{R}_5)$ , in which  $\text{R}_4$  and  $\text{R}_5$ , which may be identical or different, represent a  $\text{C}_1$  to  $\text{C}_6$  alkyl group or a phenyl group;  $\text{R}_6$  and/or  $\text{R}_7$  may especially be a methyl, ethyl, propyl, n-butyl, isobutyl, tert-butyl, hexyl, ethylhexyl, octyl, lauryl, isoctyl, isodecyl, dodecyl, cyclohexyl, t-butylcyclohexyl or stearyl group; 2-ethylperfluorohexyl; or a  $\text{C}_{1-4}$  hydroxyalkyl group such as 2-hydroxyethyl, 2-hydroxybutyl or 2-hydroxypropyl; or a  $(\text{C}_{1-4})$ alkoxy $(\text{C}_{1-4})$ alkyl group such as methoxyethyl, ethoxyethyl or methoxypropyl,
- a  $\text{C}_3$  to  $\text{C}_{12}$  cycloalkyl group, such as an isobornyl group,
- a  $\text{C}_3$  to  $\text{C}_{20}$  aryl group such as a phenyl group,
- a  $\text{C}_4$  to  $\text{C}_{30}$  aralkyl group ( $\text{C}_1$  to  $\text{C}_8$  alkyl group) such as 2-phenylethyl, t-butylbenzyl or benzyl,
- a 4- to 12-membered heterocyclic group containing one or more heteroatoms chosen from O, N and S, the ring being aromatic or non-aromatic,
- a heterocycloalkyl group (1 to 4 C alkyl), such as furfurylmethyl or tetrahydrofurfurylmethyl, said cycloalkyl, aryl, aralkyl, heterocyclic or heterocycloalkyl groups possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms and linear or branched  $\text{C}_1$ - $\text{C}_4$  alkyl groups in which is (are) optionally intercalated one or more heteroatoms chosen from O, N, S and P, said alkyl groups also possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms (Cl, Br, I and F) and groups  $\text{Si}(\text{R}_4\text{R}_5)$ , in which  $\text{R}_4$  and  $\text{R}_5$ , which may be identical or different, represent a  $\text{C}_1$  to  $\text{C}_6$  alkyl group or a phenyl group.

Examples of (meth)acrylamide monomers are (meth)acrylamide, N-ethyl(meth)acrylamide, N-butylacrylamide, N-t-butylacrylamide, N-isopropylacrylamide, N,N-dimethyl(meth)acrylamide, N,N-dibutylacrylamide, 5 N-octylacrylamide, N-dodecylacrylamide, undecylacrylamide and N(2-hydroxypropylmethacrylamide).

- (iv) the vinyl compounds of formulae:



10 in which  $\text{R}_9$  is a hydroxyl group, halogen (Cl or F),  $\text{NH}_2$ ,  $\text{OR}_{14}$  in which  $\text{R}_{14}$  represents a phenyl group or a  $\text{C}_1$  to  $\text{C}_{12}$  alkyl group (the monomer is a vinyl or allylic ether); acetamide ( $\text{NHCOCH}_3$ ); a group  $\text{OCOR}_{15}$  in which  $\text{R}_{15}$  represents a linear or branched alkyl group of 2 to 12 15 carbons (the monomer is a vinyl or allylic ester); or a group chosen from:

- a linear or branched alkyl group of 1 to 18 carbon atoms, in which is (are) optionally intercalated one or more heteroatoms chosen from O, N, S and P; said alkyl 20 group also possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms (Cl, Br, I and F) and groups  $\text{Si}(\text{R}_4\text{R}_5)$ , in which  $\text{R}_4$  and  $\text{R}_5$ , which may be identical or different, represent a  $\text{C}_1$  to  $\text{C}_6$  alkyl group or a phenyl group;
- 25 - a  $\text{C}_3$  to  $\text{C}_{12}$  cycloalkyl group such as isobornyl or cyclohexane,
- a  $\text{C}_3$  to  $\text{C}_{20}$  aryl group such as phenyl,
- a  $\text{C}_4$  to  $\text{C}_{30}$  aralkyl group ( $\text{C}_1$  to  $\text{C}_8$  alkyl group) such as 2-phenylethyl; benzyl,
- 30 - a 4- to 12-membered heterocyclic group containing one or more heteroatoms chosen from O, N and S, the ring being aromatic or non-aromatic,
- a heterocycloalkyl group (1 to 4 C alkyl), such as furfurylmethyl or tetrahydrofurfurylmethyl,
- 35 said cycloalkyl, aryl, aralkyl, heterocyclic or heterocycloalkyl groups possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms and linear or branched 1 to 4 C alkyl groups in which is (are) optionally



intercalated one or more heteroatoms chosen from O, N, S and P, said alkyl groups also possibly being optionally substituted with one or more substituents chosen from hydroxyl groups, halogen atoms (Cl, Br, I and F) and groups  $\text{Si}(\text{R}_4\text{R}_5)$  in which  $\text{R}_4$  and  $\text{R}_5$ , which may be identical or different, represent a  $\text{C}_1$  to  $\text{C}_6$  alkyl group, or a phenyl group.

Examples of vinyl monomers are vinyl cyclohexane and styrene.

Examples of vinyl esters are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl ethylhexanoate, vinyl neononanoate and vinyl neododecanoate.

Among the vinyl ethers that may be mentioned are methyl vinyl ether, ethyl vinyl ether and isobutyl vinyl ether.

- (v) (meth)acrylic, (meth)acrylamide or vinyl monomers containing a fluoro or perfluoro group, such as ethylperfluorooctyl or 2-ethylperfluorohexyl (meth)acrylate;

- (vi) silicone-based (meth)acrylic, (meth)acrylamide or vinyl monomers, such as methacryloxypropyltris(trimethylsiloxy)silane or acryloxypropylpolydimethylsiloxane;

- (vii) ethylenically unsaturated monomers comprising at least one carboxylic, phosphoric or sulfonic acid, or anhydride, function, for instance acrylic acid, methacrylic acid, crotonic acid, maleic anhydride, itaconic acid, fumaric acid, maleic acid, acrylamidopropanesulfonic acid, vinylbenzoic acid and vinylphosphoric acid, and the salts thereof;

- (viii) ethylenically unsaturated monomers comprising at least one tertiary amine function, for instance

2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and dimethylaminopropylmethacrylamide, and the salts thereof.

5

The salts may be formed by neutralization of the anionic groups with a mineral base, such as LiOH, NaOH, KOH,  $\text{Ca}(\text{OH})_2$ ,  $\text{NH}_4\text{OH}$  or  $\text{Zn}(\text{OH})_2$ ; or with an organic base such as a primary, secondary or tertiary alkylamine, especially triethylamine or butylamine. This primary, secondary or tertiary alkylamine may comprise one or more nitrogen and/or oxygen atoms and may thus comprise, for example, one or more alcohol functions; mention may be made especially of amino-2-methyl-2-propanol, triethanolamine and dimethylamino-2-propanol. Mention may also be made of lysine or 3-(dimethylamino)propylamine.

Mention may also be made of the salts of mineral acids, such as sulfuric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid or boric acid. Mention may also be made of the salts of organic acids, which may comprise one or more carboxylic, sulfonic or phosphonic acid groups. They may be linear, branched, or cyclic aliphatic acids, or alternatively aromatic acids. These acids may also comprise one or more heteroatoms chosen from O and N, for example in the form of hydroxyl groups. Mention may be made especially of propionic acid, acetic acid, terephthalic acid, citric acid and tartaric acid.

It is obviously possible to use several of the additional comonomers mentioned above.

The additional comonomer(s) may be present in an amount of from 30% to 99.99% by weight, especially in an amount of from 50% to 99.9% by weight, in particular from 70% to 99.5% by weight, or even from 80% to 99% by weight, and better still from 90% to 98% by weight,

relative to the weight of the final polymer.

The additional comonomers are more particularly chosen, alone or as a mixture, from  $C_1$ - $C_{18}$  alkyl or  $C_3$ - $C_{12}$  cycloalkyl (meth)acrylates, and especially from methyl  
5 acrylate, methyl methacrylate, isobornyl acrylate, isobornyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, dodecyl acrylate, dodecyl methacrylate,  
10 stearyl acrylate, stearyl methacrylate, trifluoroethyl acrylate and trifluoroethyl methacrylate.

Mention may also be made of acrylic acid, methacrylic acid, methacryloxypropyltris(trimethylsiloxy)silane,  
15 acryloxypropyltris(trimethylsiloxy)silane, acryloxypropylpolydimethylsiloxane and methacryloxypropylpolydimethylsiloxane.

Said polymers may be prepared according to the methods  
20 known to those skilled in the art, especially by radical polymerization; controlled radical polymerization, for example with xanthans, dithiocarbamates or dithio esters; by polymerization using precursors of nitroxide type; by atom transfer  
25 radical polymerization (ATRP); by group transfer polymerization.

The polymerization may conventionally be performed in the presence of a polymerization initiator, which may  
30 be a radical initiator, and especially which may be chosen from organic peroxide compounds such as dilauroyl peroxide, dibenzoyl peroxide, tert-butyl peroxy-2-ethylhexanoate; or from diazo compounds such as azobisisobutyronitrile or azobisdimethylvaleronitrile.  
35 nitrile. The reaction may also be initiated using photoinitiators or via radiation of UV type, with neutrons or with plasma.

The monomeric compounds with an optical effect, and

also preferably the homopolymers or copolymers comprising them, preferably have an absorption wavelength of between 200 and 550 nm, especially between 220 and 520 nm or even between 240 and 500 nm.

5

They preferably have an emission wavelength of between 350 and 750 nm, especially between 390 and 700 nm, or even between 420 and 670 nm.

10 The weight-average molecular mass (Mw) of the copolymers according to the invention is preferably between 5000 and 600 000 g/mol, especially between 10 000 and 300 000 g/mol and better still between 20 000 and 150 000 g/mol.

15

The weight-average (Mw) and number-average (Mn) molecular masses are determined by gel permeation liquid chromatography (GPC), eluting with THF, on a calibration curve established with linear polystyrene standards, using a refractometric detector and UV.

20

The polymers according to the invention, whether they are homopolymers or copolymers, may be present, alone or as a mixture, in the compositions according to the invention in an amount of from 0.01% to 60% by weight, preferably 0.1% to 50% by weight, especially 1% to 25% by weight, or even 3% to 15% by weight and better still 5% to 12% by weight, relative to the total weight of the composition.

30

They may be present in the composition in dissolved form, for example in water, in an oil or in an organic solvent, or alternatively in the form of an aqueous or organic dispersion.

35

Advantageously, the polymers according to the invention are soluble or dispersible in at least one of the phases of the composition comprising them.

The cosmetic or pharmaceutical compositions according to the invention comprise, besides said polymers, a physiologically acceptable medium, especially a cosmetically, dermatologically or pharmaceutically acceptable medium, i.e. a medium that is compatible with keratin materials such as facial or bodily skin, the hair, the eyelashes, the eyebrows and the nails.

The composition may thus comprise a hydrophilic medium comprising water or a mixture of water and hydrophilic organic solvent(s), for instance alcohols and especially linear or branched lower monoalcohols containing from 2 to 5 carbon atoms, for instance ethanol, isopropanol or n-propanol, and polyols, for instance glycerol, diglycerol, propylene glycol, sorbitol or pentylene glycol, and polyethylene glycols, or alternatively hydrophilic C<sub>2</sub> ethers and C<sub>2</sub>-C<sub>4</sub> aldehydes.

The water or the mixture of water and hydrophilic organic solvents may be present in the composition according to the invention in a content ranging from 0.1% to 99% by weight and preferably from 10% to 80% by weight relative to the total weight of the composition.

The composition may also be anhydrous.

The composition may also comprise a fatty phase which may comprise fatty substances that are liquid at room temperature (in general 25°C) and/or fatty substances that are solid at room temperature, such as waxes, pasty fatty substances and gums, and mixtures thereof. These fatty substances may be of animal, plant, mineral or synthetic origin. This fatty phase may also contain lipophilic organic solvents.

As fatty substances that are liquid at room temperature, often referred to as oils, which may be used in the invention, mention may be made of:

hydrocarbon-based oils of animal origin such as perhydrosqualene; hydrocarbon-based plant oils such as liquid triglycerides of fatty acids of 4 to 10 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively sunflower oil, maize oil, soybean oil, grapeseed oil, sesame seed oil, apricot oil, macadamia oil, castor oil, avocado oil, caprylic/capric acid triglycerides, jojoba oil, shea butter, linear or branched hydrocarbons of mineral or synthetic origin, such as liquid paraffin and derivatives thereof, petroleum jelly, polydecenes, hydrogenated polyisobutene such as parleam; synthetic esters and ethers, especially of fatty acids, for instance purcellin oil, isopropyl myristate, 2-ethylhexyl palmitate, 2-octyldodecyl stearate, 2-octyldodecyl erucate, isostearyl isostearate; hydroxylated esters, for instance isostearyl lactate, octyl hydroxystearate, octyldodecyl hydroxystearate, diisostearyl malate, triisocetyl citrate, and fatty alcohol heptanoates, octanoates and decanoates; polyol esters, for instance propylene glycol dioctanoate, neopentyl glycol diheptanoate and diethylene glycol diisononanoate; and pentaerythritol esters; fatty alcohols containing from 12 to 26 carbon atoms, for instance octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol and oleyl alcohol; partially hydrocarbon-based fluoro oils and/or partially silicone-based fluoro oils; silicone oils, for instance volatile or non-volatile, linear or cyclic polymethylsiloxanes (PDMSs), which are liquid or pasty at room temperature, for instance cyclomethicones, dimethicones, optionally comprising a phenyl group, for instance phenyl trimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenylmethyldimethyltrisiloxanes, diphenyl dimethicones, phenyl dimethicones and polymethylphenylsiloxanes; mixtures thereof.

These oils may be present in a content ranging from 0.01% to 90% and better still from 0.1% to 85% by

weight relative to the total weight of the composition.

The composition according to the invention may also  
comprise one or more physiologically acceptable organic  
5 solvents.

These solvents may be generally present in a content  
ranging from 0.1% to 90%, preferably from 0.5% to 85%,  
more preferably from 10% to 80% and better still from  
10 30% to 50% by weight, relative to the total weight of  
the composition.

Mention may be made especially, besides the hydrophilic  
organic solvents mentioned above, of ketones that are  
15 liquid at room temperature such as methyl ethyl ketone,  
methyl isobutyl ketone, diisobutyl ketone, isophorone,  
cyclohexanone and acetone; propylene glycol ethers that  
are liquid at room temperature, such as propylene  
glycol monomethyl ether, propylene glycol monomethyl  
20 ether acetate, and dipropylene glycol mono-n-butyl  
ether; short-chain esters (containing from 3 to 8  
carbon atoms in total), such as ethyl acetate, methyl  
acetate, propyl acetate, n-butyl acetate and isopentyl  
acetate; ethers that are liquid at 25°C, such as  
25 diethyl ether, dimethyl ether or dichlorodiethyl ether;  
alkanes that are liquid at 25°C, such as decane,  
heptane, dodecane, isododecane and cyclohexane;  
aromatic cyclic compounds that are liquid at 25°C, such  
as toluene and xylene; aldehydes that are liquid at  
30 25°C, such as benzaldehyde and acetaldehyde, and  
mixtures thereof.

For the purposes of the present invention, the term  
"wax" means a lipophilic compound that is solid at room  
35 temperature (25°C), which undergoes a reversible  
solid/liquid change of state, and which has a melting  
point of greater than or equal to 25°C, which may be up  
to 120°C. By bringing the wax to the liquid state  
(melting), it is possible to make it miscible with the

oils possibly present and to form a microscopically homogeneous mixture, but, on returning the temperature of the mixture to room temperature, recrystallization of the wax is obtained in the oils of the mixture. The melting point of the wax may be measured using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name DSC 30 by the company Mettler.

The waxes may be hydrocarbon-based waxes, fluoro waxes and/or silicone waxes and may be of plant, mineral, animal and/or synthetic origin. In particular, the waxes have a melting point of greater than 30°C and better still greater than 45°C. As waxes that may be used in the composition of the invention, mention may be made of beeswax, carnauba wax or candellila wax, paraffin, microcrystalline waxes, ceresin or ozokerite, synthetic waxes, for instance polyethylene waxes or Fischer-Tropsch waxes, and silicone waxes, for instance alkyl or alkoxy dimethicones containing from 16 to 45 carbon atoms.

The gums are generally polydimethylsiloxanes (PDMSs) of high molecular weight or cellulose gums or polysaccharides, and the pasty substances are generally hydrocarbon-based compounds, for instance lanolins and derivatives thereof, or PDMSs.

The nature and amount of the solid substances depend on the desired mechanical properties and textures. As a guide, the composition may contain from 0.1% to 50% by weight and better still from 1% to 30% by weight of waxes relative to the total weight of the composition.

The composition according to the invention may also comprise, in a particulate phase, pigments and/or nacles and/or fillers usually used in cosmetic compositions.



The composition may also comprise other dyestuffs chosen from water-soluble dyes and/or liposoluble dyes that are well known to those skilled in the art.

5 The term "pigments" should be understood as meaning white or colored, mineral or organic particles of any shape, which are insoluble in the physiological medium and which are intended to color the composition.

10 The term "fillers" should be understood as meaning colorless or white, mineral or synthetic, lamellar or non-lamellar particles intended to give body or rigidity to the composition, and/or softness, a matt effect and uniformity to the makeup result.

15 The term "nacles" should be understood as meaning iridescent particles of any form, produced especially by certain molluscs in their shell, or else synthesized.

20 The pigments may be present in the composition in a proportion of from 0.01% to 25% and preferably in a proportion of from 3% to 10% by weight of the final composition. They may be white or colored, and mineral  
25 or organic. Mention may be made of titanium oxide, zirconium oxide or cerium oxide, and also zinc oxide, iron oxide or chromium oxide, ferric blue, chromium hydrate, carbon black, ultramarines (aluminosilicate polysulfides), manganese pyrophosphate and certain  
30 metallic powders such as silver or aluminum powder. Mention may also be made of the D&C pigments and lakes commonly used to give the lips and the skin a makeup effect, which are calcium, barium, aluminum, strontium or zirconium salts.

35 The nacles may be present in the composition in a proportion of from 0.01% to 20% by weight and preferably in a proportion of about from 3% to 10% by weight. Among the nacles that may be envisaged, mention

may be made of natural mother-of-pearl, mica coated with titanium oxide, with iron oxide, with natural pigment or with bismuth oxychloride, and also colored titanium mica.

5

Among the liposoluble or water-soluble dyes that may be present in the composition, alone or as a mixture, in a proportion of from 0.001% to 15% by weight, preferably 0.01% to 5% by weight and especially from 0.1% to 2% by weight, relative to the total weight of the composition, mention may be made of the disodium salt of ponceau, the disodium salt of alizarin green, quinoline yellow, the trisodium salt of amaranth, the disodium salt of tartrazine, the monosodium salt of rhodamine, the disodium salt of fuchsin, xanthophyll, methylene blue, cochineal carmine, halo-acid dyes, azo dyes, anthraquinone dyes, copper sulfate, iron sulfate, Sudan brown, Sudan red and annatto, and also beetroot juice and carotene.

20

The composition according to the invention may also comprise one or more fillers, especially in a content ranging from 0.01% to 50% by weight and preferably ranging from 0.02% to 30% by weight, relative to the total weight of the composition. The fillers may be mineral or organic in any form, platelet-shaped, spherical or oblong. Mention may be made of talc, mica, silica, kaolin, polyamide (Nylon®) powder, poly- $\beta$ -alanine powder and polyethylene powder, powders of tetrafluoroethylene polymers (Teflon®), lauroyllysine, starch, boron nitride, hollow polymer microspheres such as those of polyvinylidene chloride/acrylonitrile, for instance Expancel® (Nobel Industrie), of acrylic acid copolymers (Polytrap® from the company Dow Corning) and silicone resin microbeads (for example Tospearls® from Toshiba), elastomeric polyorganosiloxane particles, precipitated calcium carbonate, magnesium carbonate, magnesium hydrocarbonate, hydroxyapatite, hollow silica microspheres (Silica Beads® from Maprecos), glass or

ceramic microcapsules, and metal soaps derived from organic carboxylic acids containing from 8 to 22 carbon atoms and preferably from 12 to 18 carbon atoms, for example zinc, magnesium or lithium stearate, zinc  
5 laurate or magnesium myristate.

The composition may also comprise an additional polymer such as a film-forming polymer. According to the present invention, the term "film-forming polymer"  
10 means a polymer capable, by itself or in the presence of an auxiliary film-forming agent, of forming a continuous film that adheres to a support and especially to keratin materials. Among the film-forming polymers that may be used in the composition of the  
15 present invention, mention may be made of synthetic polymers, of free-radical type or of polycondensate type, polymers of natural origin and mixtures thereof, in particular acrylic polymers, polyurethanes, polyesters, polyamides, polyureas and cellulose-based  
20 polymers, for instance nitrocellulose.

The composition according to the invention may also comprise ingredients commonly used in cosmetics, such as vitamins, thickeners, gelling agents, trace  
25 elements, softeners, sequestrants, fragrances, acidifying or basifying agents, preserving agents, sunscreens, surfactants, antioxidants, hair-loss counteractants, antidandruff agents, propellants and ceramides, or mixtures thereof. Needless to say, a  
30 person skilled in the art will take care to select this or these optional additional compound(s), and/or the amount thereof, such that the advantageous properties of the composition according to the invention are not, or are not substantially, adversely affected by the  
35 envisaged addition.

The composition according to the invention may be in the form of a suspension, a dispersion, especially of oil in water by means of vesicles; an optionally

thickened or even gelled oily solution; an oil-in-water, water-in-oil or multiple emulsion; a gel or a mousse; an oily or emulsified gel; a dispersion of vesicles, especially of lipid vesicles; a two-phase or  
5 multiphase lotion; a spray; a loose, compact or cast powder; an anhydrous paste. This composition may have the appearance of a lotion, a cream, a pomade, a soft paste, an ointment, a cast or molded solid especially as a stick or in a dish, or alternatively a compacted  
10 solid.

A person skilled in the art will be able to choose the appropriate galenical form, and also the method for preparing it, on the basis of his general knowledge,  
15 taking into account firstly the nature of the constituents used, especially their solubility in the support, and secondly the intended application of the composition.

20 The cosmetic composition according to the invention may be in the form of a care and/or makeup product for bodily or facial skin, the lips, the nails, the eyelashes, the eyebrows and/or the hair, an antison or self-tanning product, or a hair product for caring for,  
25 treating, shaping, making up or dyeing the hair.

It may also be in the form of a makeup composition, especially a complexion product such as a foundation, a makeup rouge or an eyeshadow; a lip product such as a  
30 lipstick or a lipcare product; a concealer product; a blusher, a mascara or an eyeliner; an eyebrow makeup product, a lip pencil or an eye pencil; a nail product such as a nail varnish or a nailcare product; a body makeup product; a hair makeup product (hair mascara or  
35 hair lacquer).

It may also be in the form of a composition for protecting or caring for the skin of the face, the neck, the hands or the body, especially an antiwrinkle

composition or a moisturizing or treating composition;  
an antisen composition or artificial tanning  
composition.

5 It may also be in the form of a hair product,  
especially for dyeing, holding the hairstyle, shaping  
the hair, caring for, treating or cleansing the hair,  
such as shampoos, hairsetting gels or lotions, blow-  
drying lotions, and fixing and styling compositions  
10 such as lacquers or sprays.

A subject of the invention is also a cosmetic process  
for making up or caring for keratin materials,  
especially bodily or facial skin, the lips, the nails,  
15 the eyelashes, the eyebrows and/or the hair, comprising  
the application to said materials of a cosmetic  
composition as defined above.

The invention is illustrated in greater detail in the  
20 examples that follow.

Method for measuring the wavelength (emission and  
absorption)

25 The wavelength measurement is performed using a Varian  
Cary Eclipse fluorimeter.

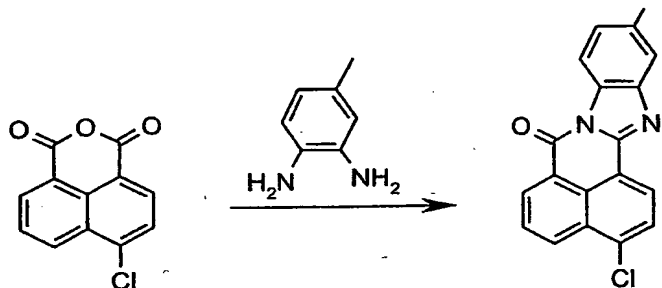
Unless otherwise mentioned, this measurement is  
performed in the following manner: 20 mg of product are  
30 placed in a 50 ml cylinder. To dissolve the product,  
said cylinder is filled to 50 ml with a suitable  
solvent, for example dichloromethane (DCM), chloroform  
or dimethyl sulfoxide (DMSO). The resulting solution is  
mixed and 250 microliters are taken and placed in a  
35 50 ml cylinder, and the volume is then made up to 50 ml  
again with the solvent.

The whole is mixed and a sample of the solution is  
taken and placed in a closed quartz cell 10 mm thick,

which is then placed in the measuring chamber.

Example 1

5 1. First step

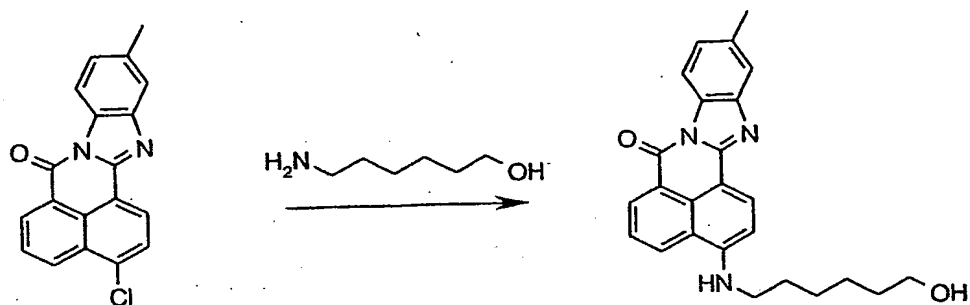


179.9 g (0.77 mol) of 4-chloro-1,8-naphthalic anhydride  
10 are placed in a 1-liter three-necked flask, under an  
inert atmosphere (nitrogen), followed by addition of  
1 liter of 2-(2-ethoxyethoxy)ethanol. The mixture is  
heated to 100°C and becomes clear orange. 100 g  
(0.78 mol) of 3,4-diaminotoluene predissolved in 300 ml  
15 of 2-(2-ethoxyethoxy)ethanol are added dropwise, with  
stirring. The addition funnel is rinsed with 200 ml of  
this solvent. The reaction solution is heated at 150°C  
for 18 hours. The resulting reaction mixture is then  
allowed to cool to room temperature. The precipitate is  
20 filtered off through a sinter funnel and then washed  
with ethanol. It is recovered and dried under vacuum.  
211.3 g of orange crystals are obtained (72.6% yield).

Characterization

25 <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 8.74-8.72 (1H), 8.61-8.42  
(3H), 7.83-7.56 (3H), 7.24-7.22 (1H), 2.54-2.51 (3H).

2. Second step

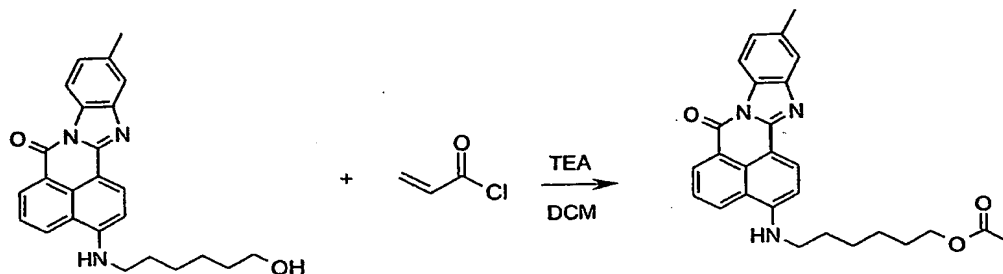


13.6 g (42.7 mmol) of p-tolyl-4-chloroisoquinolinone are placed in a three-necked flask equipped with a Dimroth condenser and placed under an inert atmosphere of argon, and 100.0 g (0.85 mol) of 6-amino-1-hexanol are added. The mixture is heated to 180°C with stirring to obtain a homogeneous mixture; it is left to react for 16 hours and is then cooled to room temperature, and a red precipitate forms. Said precipitate is filtered off and washed with ethanol. 17.0 g of desired product are obtained.

#### Characterization

<sup>1</sup>H NMR (DMSO, 400MHz) δ: 8.82-8.20 (4H), 7.96-7.49 (3H), 7.28-7.15 (1H), 6.82-6.80 (1H), 4.37 (1H), 3.41-3.39 (2H), 2.49-2.45 (5H), 1.72-1.69 (2H), 1.48-1.35 (6H).

#### 3. Third step



5.0 g (12.5 mmol) of p-tolyl-4-(6-hexanol)isoquinolinone are placed in a three-necked flask equipped with a Dimroth condenser, and placed under an inert atmosphere of argon. 150 ml of dry dichloromethane are

added and the mixture is stirred until a homogeneous solution is obtained. 7.0 ml (50 mmol) of triethanolamine are then added, followed by addition of 4.1 ml (50 mmol) of acryloyl chloride, with stirring at 0°C. The temperature is allowed to rise to 25°C. The reaction progress is monitored by TLC, and, when it is observed that the reaction is complete, 50 ml of water are added. The reaction solution is then washed with salt water + sodium bicarbonate (brine) and then with water again, and dried over sodium sulfate. The solvents are evaporated off under reduced pressure to give 4.1 g (73.5% yield) of a red powder.

#### Characterization

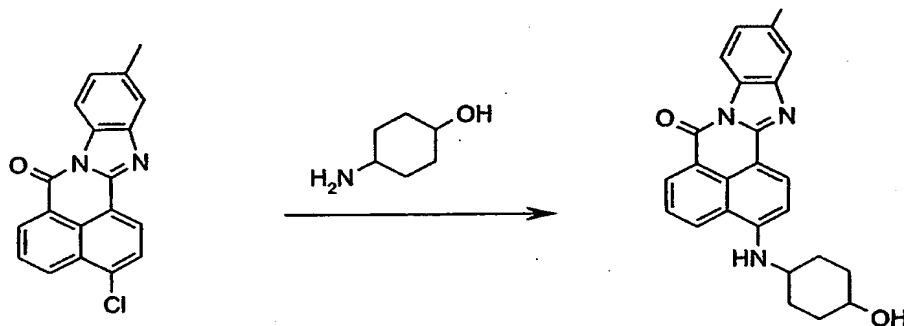
<sup>1</sup>H NMR (DMSO, 500MHz)  $\delta$ : 8.70-8.68 (1H), 8.63-8.60 (1H), 8.44-8.42 (1H), 8.33-8.29 (1H), 7.90-7.88 (1H), 7.73-7.61 (2H), 7.27-7.23 (1H), 6.82-6.81 (1H), 6.32-6.29 (1H), 6.18-6.12 (1H), 5.92-5.89 (1H), 4.13-4.11 (2H), 3.41-3.37 (2H), 1.74-1.62 (4H), 1.47-1.40 (4H).

$\lambda_{\text{max}}$  absorption: 377 nm

$\lambda_{\text{max}}$  emission: 556 nm (red)

#### 25 Example 2

##### 1. First step



30

8.0 g (25.1 mmol) of p-tolyl-4-chloroisoquinolinone and 8.7 g of trans-aminocyclohexanol (75.3 mmol, 3 eq) are



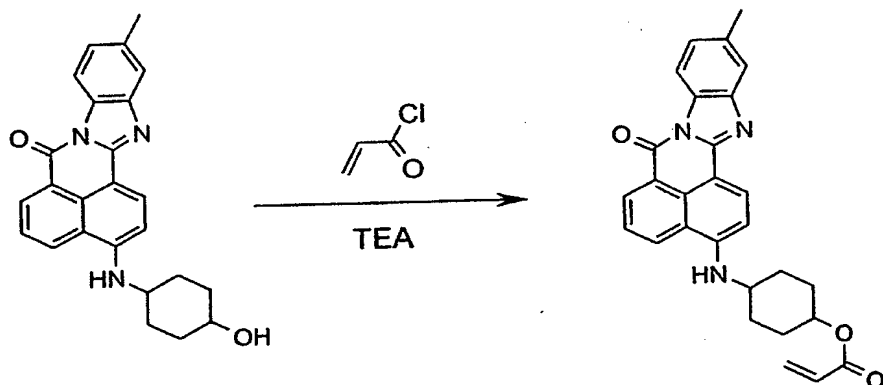
placed in a microwave reactor. 30 ml of NMP are added. The reactor is placed in a microwave tank with a glass stirring paddle. The mixture is heated with stirring to 130°C over 5 minutes and then maintained at 130°C for 4 hours. The solid medium slowly becomes liquid and changes from a pasty yellow-green solution to a liquid Bordeaux-red solution. TLC is performed (9/1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to check the end of the reaction. The reaction solution is then poured into 600 ml of sodium hydrogen carbonate solution; the product precipitates immediately. It is washed three times with 600 ml of water and then dried under vacuum to give 9.07 g of a bright Bordeaux-red powder (90.9% yield).

15 Characterization

<sup>1</sup>H NMR (DMSO, 400MHz) δ: 8.89-8.65 (2H), 8.50-8.42 (1H), 8.34-8.23 (1H), 7.76-7.18 (4H), 6.94-6.91 (1H), 4.65 (1H), 3.66-3.63 (1H), 3.52-3.47 (1H), 2.51-2.47 (3H), 2.09-2.02 (2H), 1.94-1.92 (2H), 1.55-1.37 (4H).

20

2. Second step



25 10.0 g (25 mmol) of p-tolyl-4-cyclohexylamino-4-hydroxyisoquinolinone are placed in a 1-liter three-necked flask, under an inert atmosphere (argon), and 350 ml of dichloromethane are then added. The mixture is stirred until a homogeneous solution is obtained.

30 3.31 g (33 mmol) of triethanolamine are then added. 3.0 g (33 mmol) of acryloyl chloride in 50 ml of

dichloromethane are added dropwise with stirring (500 rpm) at 5°C, and the reaction solution is then heated to 40°C. The reaction is monitored by TLC until the starting material has disappeared. After reaction for 3 hours, the organic phase is washed with water and sodium bicarbonate, and then again with water. The organic phase is dried over sodium sulfate and the solvents are evaporated off. The crude product obtained is purified on silica. 5.1 g of the desired product are recovered.

#### Characterization

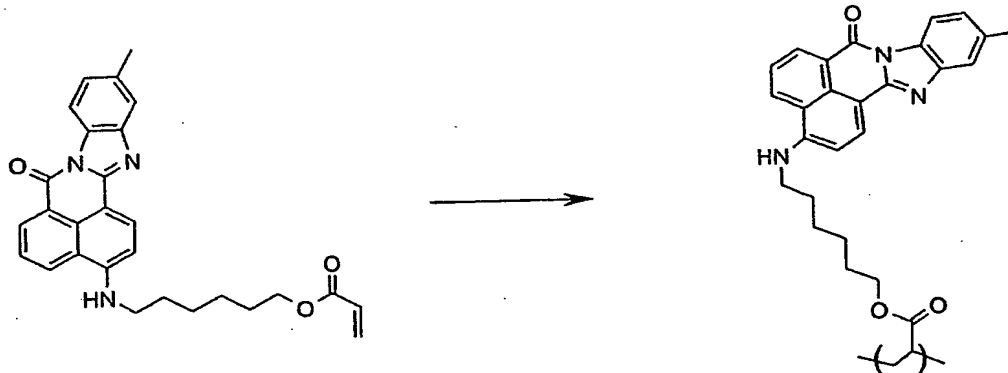
<sup>1</sup>H NMR (DMSO, 400MHz) δ: 8.89-8.65 (2H), 8.50-8.42 (1H), 8.34-8.23 (1H), 7.76-7.18 (4H), 6.94-6.91 (1H), 6.37-6.32 (1H), 6.23-6.16 (1H), 5.96-5.94 (1H), 4.79-4.76 (1H), 3.75-3.74 (1H), 2.49-2.45 (3H), 2.11-2.05 (4H), 1.68-1.58 (4H).

λ<sub>max</sub> absorption: 472 nm

λ<sub>max</sub> emission: 587 nm

#### Example 3

A homopolymer according to the invention is prepared from a monomer of example 1.



1.0 g (2.2 mmol) of monomer prepared in example 1 is dissolved in 15 ml of anhydrous THF, at 60°C, in the presence of 180 μl of polymerization initiator (Trigonox 21S). The mixture is heated to 90°C with stirring and stirring is then continued for 20 hours.

The viscosity of the solution increases; the medium is diluted by adding 20 ml of THF and is then precipitated dropwise from 500 ml of acetone cooled to 0°C. The polymer obtained is dried in an oven (50°C) under reduced pressure.

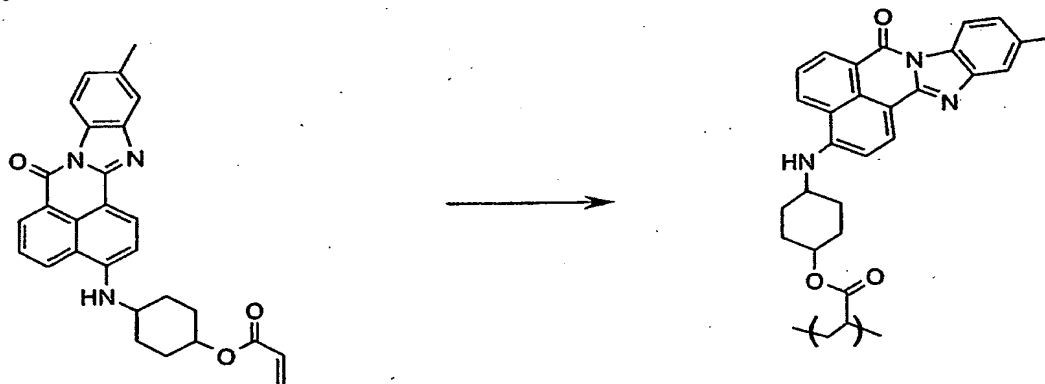
0.56 g of homopolymer is obtained (yield: 56%).

$\lambda_{\text{max}}$  absorption: 578 nm

$\lambda_{\text{max}}$  emission: 620 nm

#### Example 4

A homopolymer according to the invention is prepared from the monomer of example 2.



15

1.0 g (2.2 mmol) of monomer prepared in example 2 is dissolved in 15 ml of anhydrous THF, at 60°C, in the presence of 180  $\mu$ l of polymerization initiator (Trigonox 21S). The mixture is heated to 90°C with stirring and stirring is then continued for 18 hours. The viscosity of the solution increases; the medium is diluted by adding 20 ml of THF and is then precipitated dropwise from 500 ml of acetone cooled to 0°C. The polymer obtained is dried in an oven (50°C) under reduced pressure.

0.54 g of homopolymer is obtained (yield: 54%).

$\lambda_{\text{max}}$  absorption: 472 nm

30  $\lambda_{\text{max}}$  emission: 587 nm

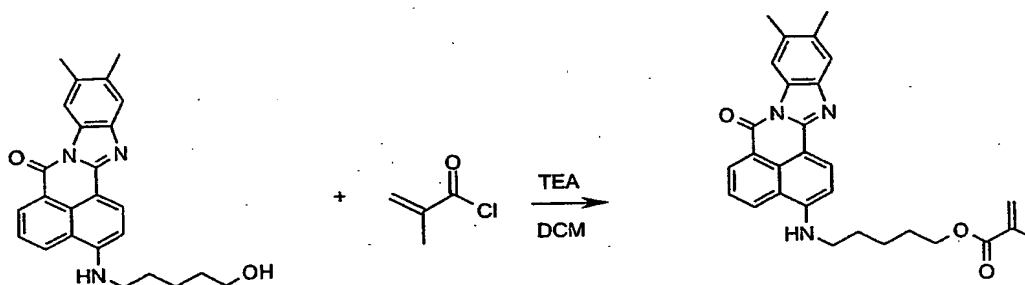
### Example 5

A statistic copolymer according to the invention is prepared.

5

4 g of the monomer prepared in example 1 are dissolved in 20 g of DMSO, and isobornyl acrylate (33 g), isobornyl methacrylate (33 g), isobutyl acrylate (30 g), isododecane (80 g) and 1 g of initiator 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel) are then added. The mixture is heated to 120°C and maintained at this temperature for 4 hours. The mixture is then allowed to cool to room temperature and, after replacing the DMSO with isododecane, a solution with a polymer solids content of 50% in isododecane is obtained. This polymer has a weight-average mass of 43 600 and a polydispersity index  $I_p$  of 6.8.

### 20 Example 6



4.0 g (10.01 mmol) of dimethylbenzoisquinolinoneamino-  
25 pentanol are placed in a three-necked flask equipped with a Dimroth condenser and placed under an inert atmosphere of argon. 200 ml of dry dichloromethane (DCM) are added and the mixture is stirred until a homogeneous solution is obtained. 3 g (30 mmol) of  
30 triethanolamine are then added, followed by addition of 1.9 g (18.0 mmol) of methacryloyl chloride diluted in 15 ml of DCM, with stirring at 45°C. The reaction progress is monitored by TLC. When it is observed that

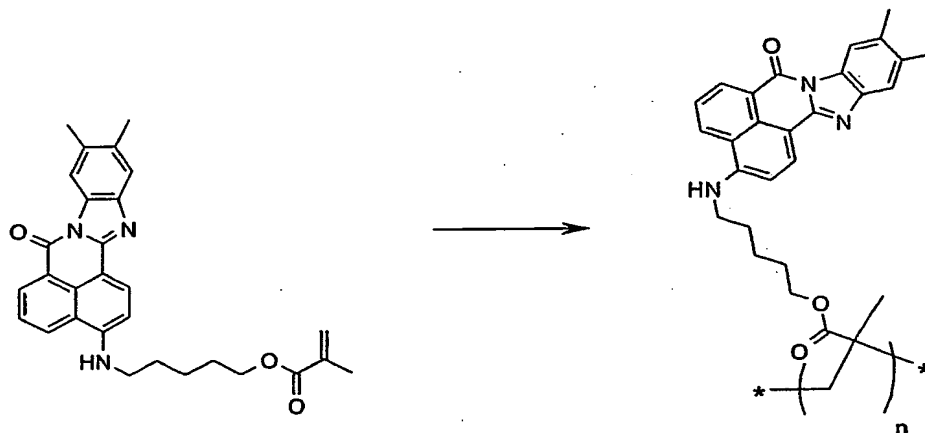
the reaction is complete (about 24 hours), the reaction solution is washed with salt water + sodium bicarbonate (brine) and then with water again, and is dried over sodium sulfate. The solvents are evaporated off under reduced pressure to give 1.64 g (35% yield) of an orange-red powder.

#### Characterization

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 8.63-8.60 (1H), 8.40-8.25 (2H), 7.82-7.79 (1H), 7.58-7.47 (2H), 6.53-6.50 (1H), 6.11 (1H), 5.57-5.56 (1H), 5.23-5.20 (1H), 4.21-4.17 (2H), 3.20-3.15 (2H), 2.44-2.37 (6H), 1.95 (3H), 1.75-1.66 (4H), 1.53-1.45 (2H).

#### Example 7

A homopolymer according to the invention is prepared from the monomer of example 6.



20

0.5 g (1.07 mmol) of monomer prepared in example 6 is dissolved in 25 ml of anhydrous THF, at 90°C, in the presence of 0.05 g of polymerization initiator (Trigonox 141S). The mixture is heated to 90°C with stirring and is then maintained at this temperature for 30 hours. The polymer is precipitated dropwise from 500 ml of acetone cooled to -10°C. The polymer obtained is dried in an oven (60°C) under reduced pressure.

0.13 g of homopolymer is obtained in the form of an orange powder.

Example 8

5

A statistical copolymer according to the invention is prepared.

6 g of the monomer prepared in example 1 are dissolved  
10 in 60 ml of THF, at 60°C, and 14 g of 2-ethylhexyl  
acrylate and 10 ml of isododecane are then added. The  
mixture is heated at 80°C with stirring for 30 minutes,  
and 0.4 g of initiator (Trigonox 21S) diluted with  
10 ml of THF and 5 ml of isododecane is then added. The  
15 mixture is heated to 90°C and maintained at this  
temperature for 24 hours. The mixture is then allowed  
to cool to room temperature and, after replacing the  
THF with isododecane, a solution with a polymer solids  
content of 50% in isododecane is obtained.

20

Example 9

An anhydrous foundation is prepared, comprising  
(weight %):

25

- polyethylene wax	12%
- volatile silicone oils	25%
- phenyl trimethicone	20%
- polymethyl methacrylate microspheres	12%
30 - polymer of example 5	6% AM
- isododecane	qs 100%

(AM: active material)

35

Preparation: The waxes are melted and, when the whole  
is clear, the phenyl trimethicone and the silicone oils  
are added with stirring; the microspheres, the  
isododecane and the polymer are then added. The mixture  
is homogenized for 15 minutes and the resulting  
composition is cast and allowed to cool. An anhydrous

foundation is obtained.

**Example 10**

- 5 A statistical copolymer comprising a monomer according to the invention is prepared.

20 g of isododecane are placed in a reactor, under argon, equipped with a condenser and a stirrer,  
10 followed by addition of 27 g of methyl methacrylate, 17 g of methyl acrylate and 5 g of acrylic acid. The mixture is stirred and a mixture consisting of 1 g of monomer from example 2 in 20.0 g of toluene is added.

0.5 g of Trigonox 21S (t-butyl peroxy-2-ethylhexanoate)  
15 is added and the reaction mixture is then heated to 90°C; stirring and heating are continued for 6 hours and the mixture is then cooled to room temperature. The resulting polymer is purified by precipitation.

A statistical polymer comprising (weight %): 54% methyl  
20 methacrylate, 34% methyl acrylate, 10% acrylic acid and 2% monomer according to the invention is obtained.

**Example 11**

- 25 A nail varnish is prepared, comprising:
- 5% by weight of polymer according to example 7
  - qs 100% organic solvents.